

## PATENT SPECIFICATION

NO DRAWINGS

853,640



Date of Application and filing Complete Specification: Jan. 30, 1959.

No. 3440/59.

Application made in Germany on Jan. 30, 1958.

Application made in Germany on June 3, 1958.

Complete Specification Published: Nov. 9, 1960.

SPECIFICATION NO. 853,640

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are Herbert Bartl, of Hahnenweg 1, Köln-Stammheim, Germany and Julius Peter, of Buchmühle, Odenthal/Berg. - Gladbach, Germany, both German citizens.

THE PATENT OFFICE,  
28th November, 1960

DS 83120/1(5)/850S 200 11/60 DL

PATENTS ACT, 1949SPECIFICATION NO. 853,640

Reference has been directed, in pursuance of Section 6, of the Patents Act, 1949, to Specification No. 866,001.

THE PATENT OFFICE,  
19th September, 1962

DS 66974/1(5) R.109 200 6/62 PL

15 linked plastics by the use of organic peroxides is known. However, the degree of cross-linking thus produced is small, so that the solubility and softening point of the material are only slightly altered. Moreover, such a cross-linked polyethylene does not have the character of an elastomeric material.

20 According to the present invention there is now provided a process for the production of cross-linked elastomers, which comprises heating a mixture of (1) a linear co-polymer of ethylene and 10 to 60 per cent by weight of a monoethylenically unsaturated monomer containing an aliphatic carbon atom having only one hydrogen atom bonded thereto, (2) 1 to 30 10 per cent by weight of said co-polymer of a free-radical forming compound and (3) 0.5 to 20 per cent by weight of said co-polymer of a monomer having at least two ethylenically unsaturated groups, at a temperature of from 35 50° C. to 250° C.

Suitable monoethylenically unsaturated monomers containing an aliphatic carbon atom having only one hydrogen atom bonded thereto and which are suitable for employ-

acid anhydride.

The copolymers can be produced by processes known *per se*. Vulcanisation products having particularly good mechanical properties are, however, produced if copolymers of ethylene and organic vinyl esters are used, which copolymers are advantageously produced by free-radical polymerisation in a liquid phase containing predominantly tertiary butanol, as described in our co-pending Application No. 204/58 (Serial No. 843,974).

65 Examples of vinyl esters which can be copolymerised with ethylene are: vinyl chloracetate, vinyl formate, vinyl benzoate and, most advantageously, vinyl acetate and vinyl propionate. Further suitable copolymers are those of ethylene and propylene. The content of the copolymerisation components, such as the vinyl esters, incorporated by polymerisation into the copolymers should be from 10 to 60 per cent by weight, and most advantageously from 20 to 50 per cent by weight.

75 As free radical formers which decompose at elevated temperature, it is possible to use persulphates, perborates, readily decompos-



# PATENT SPECIFICATION

NO DRAWINGS

853,640

Date of Application and filing Complete Specification: Jan. 30, 1959.  
No. 3440/59.

Application made in Germany on Jan. 30, 1958.

Application made in Germany on June 3, 1958.

Complete Specification Published: Nov. 9, 1960.

Index at acceptance:—Class 2(6), P4(A:C8C), P4D(1A:2:3A:3B1:3B3:8), P4K(4:6:7:8:9:11), P4P(1D:1E1:3:6D:6X), P4T2A, P6(A:C8C), P6D(3:4), P6K(4:7:8:9:10), P6P6(D:X), P6T2A, P7(A:C8C), P7D(1A:1X:2A1:2A2B:2B:3:8), P7K(4:6:7:8:9:10:11), P7P(1D:1E1:3:6D:6X), P7T2A, P8(A:C8C), P8D(1A:2A:2B2:3A:4:5), P8K(4:6:7:8:9:11), P8P6(D:X), P8T2A, P9(A:C8C), P9D(1A1:1B1:3), P9K(4:6:7:8:9:11), P9P6(D:X), P9T2A, P10(A:C8C:D1A), P10K(4:6:7:8:9:11), P10P6(D:X), P10T2A, P11(A:C8C), P11D(2A:4:7), P11K(4:7:8:9:10), P11P6(D:X), P11T2A.

International Classification:—C08f.

## COMPLETE SPECIFICATION

### Process for the Production of Cross-Linked Elastomers

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, of Leverkusen - Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for producing rubber-like polymers, and more particularly to the cross-linking of co-polymers of ethylene by means of free radical-forming compounds.

The conversion of polyethylene into cross-linked plastics by the use of organic peroxides is known. However, the degree of cross-linking thus produced is small, so that the solubility and softening point of the material are only slightly altered. Moreover, such a cross-linked polyethylene does not have the character of an elastomeric material.

According to the present invention there is now provided a process for the production of cross-linked elastomers, which comprises heating a mixture of (1) a linear co-polymer of ethylene and 10 to 60 per cent by weight of a monoethylenically unsaturated monomer containing an aliphatic carbon atom having only one hydrogen atom bonded thereto, (2) 1 to 10 per cent by weight of said co-polymer of a free-radical forming compound and (3) 0.5 to 20 per cent by weight of said co-polymer of a monomer having at least two ethylenically unsaturated groups, at a temperature of from 50° C. to 250° C.

Suitable monoethylenically unsaturated monomers containing an aliphatic carbon atom having only one hydrogen atom bonded thereto and which are suitable for employ-

ment in the process according to the present invention are esters of acrylic acid with saturated monohydric alcohols having from 1 to 8 carbon atoms (such as methanol, ethanol, propanol, butanol or cyclohexanol) acrylamide, acrylonitrile, acrylic acid, esters and semi esters of alpha-beta-monoethylenically unsaturated dicarboxylic acids (such as fumaric acid or maleic acid) with saturated monohydric alcohols having from 1 to 8 carbon atoms, monovinylaromatic compounds (such as styrene), vinyl chloride, methacrylic acid esters of secondary monohydric saturated alcohols (such as isopropanol), and also maleic acid anhydride.

The copolymers can be produced by processes known *per se*. Vulcanisation products having particularly good mechanical properties are, however, produced if copolymers of ethylene and organic vinyl esters are used, which copolymers are advantageously produced by free-radical polymerisation in a liquid phase containing predominantly tertiary butanol, as described in our co-pending Application No. 204/58 (Serial No. 843,974).

Examples of vinyl esters which can be copolymerised with ethylene are: vinyl chloracetate, vinyl formate, vinyl benzoate and, most advantageously, vinyl acetate and vinyl propionate. Further suitable copolymers are those of ethylene and propylene. The content of the copolymerisation components, such as the vinyl esters, incorporated by polymerisation into the copolymers should be from 10 to 60 per cent by weight, and most advantageously from 20 to 50 per cent by weight.

As free radical formers which decompose at elevated temperature, it is possible to use persulphates, perborates, readily decompos-

- able azo compounds, such for example as azodiisobutyronitrile or azodicarboxylic acid esters, or peroxides, such as benzoyl peroxide, dichlorobenzoyl peroxide, tertiary butyl hydroperoxide, peroxy dicarbonates, cyclohexanone peroxide, tertiary butyl perbenzoate or polyfunctional peroxides, such for example as polymeric phthalyl peroxide, adipic acid-bis-tertiary butyl perester or polyacrylic acid-tertiary butyl perester. However, peroxides which have such a low decomposition velocity at temperatures below 100° C. that they do not produce any cross-linking on being incorporated into the polymers, but decompose rapidly at higher temperatures up to 250° C., are particularly suitable. Examples of suitable peroxides conforming to those requirements are di-tertiary butyl peroxide and dicumyl peroxide, the decomposition velocities of which at temperatures below 100° C. are so low that the half-life periods of the peroxide decomposition exceed 24 hours.
- The free-radical formers are added in quantities of from 1 to 10 per cent by weight to the other components and admixed with the latter, such as by rolling or kneading. After shaping, the cross-linking is effected by heating the mixture at elevated temperatures ranging from 50° C. up to 250° C., and preferably between 100 and 200° C., for about 5 to 40 minutes.
- Examples of monomers having at least two ethylenically unsaturated groups and which are suitable for employment in the process according to the present invention are: aromatic compounds which contain at least 2 vinyl groups, such for example as divinyl benzene and trivinyl benzene, esters of polyhydric alcohols with olefinically unsaturated carboxylic acids, such for example as ethylene glycol dimethacrylate, esters of polybasic acids with olefinically unsaturated alcohols, such for example as diallyl phthalate, *o*-silicic acid tetraallyl ester and triallyl phosphate, olefinically unsaturated polyethers, such for example as diallyl and triallyl ethers of glycerine and tetraallyl or hexallyl ethers of tetramethylol or hexamethylol melamine, and polyurethanes derived from polyisocyanates and olefinically unsaturated alcohols, such for
- example as the polyurethanes obtained from polyisocyanates and allyl alcohol, olefinically unsaturated polyesters obtained from glycols and olefinically unsaturated dicarboxylic acids, such for example as maleic acid or fumaric acid, or triacrylyl perhydro-s-triazine, triallyl cyanurate or triallyl phosphate. These compounds are used in quantities of from 0.5 to 20 per cent by weight, and more especially of from 1 to 10 per cent, based on the weight of the copolymers.
- Fillers can be admixed with the copolymers, whereby a considerable improvement in the mechanical values of the vulcanisates can be produced. Pigments, colouring agents, plasticisers, age resistors, etc., can also be admixed.
- The products produced by the process of the present invention can be cross-linked to such a degree that, in contrast to the initial materials, they are practically insoluble in organic solvents. They have a substantially improved thermal stability. As one property which is of particular value, it is however to be emphasised that the products have a rubber-like elasticity, such as cannot be produced by cross-linking pure polyethylene. In addition, the copolymers have a better compatibility with other synthetic resins and natural and synthetic rubbers. The cross-linked copolymers can be used for many different purposes. For example, they are suitable for the manufacture of moulded articles such as liquid containers, pipes and flexible tubes, and are useful as coating materials, for example for the manufacture of heavy electric cables, as anti-corrosion coatings, as white wall surfacings for automobile tyres, as textile coatings, for example for rain-proof clothing and tent materials, etc., the good resistance of the products to atmospheric influences, and more especially to ozone and light, having proved particularly advantageous.
- In the following Examples, which further illustrate the invention, the parts indicated are parts by weight.
- EXAMPLE 1
- The following basic mixtures were prepared from a given copolymer of 55 per cent ethylene and 45 per cent vinyl acetate:

	A	B	C
Polymer	100	100	100
H.A.F. carbon black	50	—	—
F.T. carbon black	—	50	—
Pyrogenically obtained highly active silica	—	—	15

5 From these basic mixtures, one mixture was produced in each case with 1.2 parts of dicumyl peroxide and one mixture in each case with 1.2 parts of dicumyl peroxide and 3 parts of triallyl cyanurate.

After vulcanising for 60 minutes at a pressure of 4.0 atm. and a temperature of 151°

C., the following figures were obtained for the tension value at 300 per cent elongation and for the compression set after 70 hours at 100° C., which figures clearly show the difference in the degree of vulcanisation of the respective vulcanisates.

10

	Tension value 300 per cent	Compression Set
A: dicumyl peroxide	82 kg/cm <sup>2</sup>	17.5 per cent
dicumyl peroxide + triallyl cyanurate	102 "	4.0 "
B: dicumyl peroxide	90 "	21 "
dicumyl peroxide + triallyl cyanurate	123 "	3 "
C: dicumyl peroxide	25 "	34 "
dicumyl peroxide + triallyl cyanurate	70 "	9 "

15

## EXAMPLE 2

A copolymer of 65 per cent ethylene and 35 per cent vinyl acetate gave similar results in the same types of mixture after vulcanising

for 60 minutes at a pressure of 4.0 atm. and a temperature of 151° C., as will be seen 20 from the following Table:

	Tensile value 300 per cent	Compression Set
A: dicumyl peroxide	134 kg/cm <sup>2</sup>	20 per cent
dicumyl peroxide + triallyl cyanurate	155 "	3 "
C: dicumyl peroxide	48 "	37 "
dicumyl peroxide + triallyl cyanurate	102 "	4 "

## EXAMPLE 3

From a copolymer consisting of 55 per cent

ethylene and 45 per cent vinyl acetate, the 25 following mixtures were prepared:

	D	E
Polymer	100	100
Pyrogenically obtained highly active silica	15	15
Dicumyl peroxide	1.2	1.2
Ethylene glycol dimethacrylate	—	3

After vulcanisation for 30 minutes at a pressure of 4.0 atm. and a temperature of 151° C., the following physical values are obtained:

	D	E
Strength (kg/cm <sup>2</sup> )	96	139
Elongation (per cent)	700	595
Tension value (modulus)		
300 per cent	23	46
500 per cent	46	92
Hardness (shore) at 20° C.	55	60
Elasticity at 20° C.	43	46

#### EXAMPLE 4

From a polymer consisting of 70 per cent ethylene, 15 per cent vinyl acetate and 15 per

cent vinyl alcohol, the following mixtures were prepared:

	F	G
Polymer	100	100
Pyrogenically obtained highly active silica	15	15
Dicumyl peroxide	1.2	1.2
Triallyl cyanurate	—	3

After vulcanising for 30 minutes at a pressure of 4.0 atm. and a temperature of 151° C., the following mechanical values are obtained:

	F	G
Strength (kg/cm <sup>2</sup> )	107	205
Elongation (per cent)	130	300
Tension value 300 per cent (kg/cm <sup>2</sup> )	—	188
Shore hardness at 20° C.	93	95
75° C.	65	81
Elasticity (per cent)		
at 20° C.	31	32
at 75° C.	46	55

#### EXAMPLE 5

The following mixtures were obtained from a co-polymer of

80.0 parts by weight of ethylene and 20.0 parts by weight of vinylacetate

	H	J
polymer	100.0	100.0
pyrogenically obtained highly active silicic acid	15.0	15.0
triallyl phosphate	—	3.0
di-cumyl peroxide	2.0	2.0

After vulcanisation at 151° C. for 30 min. the following mechanical values were found:

Tensile strength (kg/cm <sup>2</sup> )	80	175
Elongation (per cent)	150	380
Modulus at 300 per cent elongation (kg/cm <sup>2</sup> )	—	128
Hardness at 20° C. (shore)	83	86
at 75° C. (shore)	75	84
Elasticity (per cent) 20° C.	38	44

#### EXAMPLE 6

5 The following mixtures were obtained  
from a co-polymer of

70.0 parts by weight of ethylene and  
30.0 parts by weight of vinylacetate

	K	L
Polymer	100.0	100.0
pyrogenically obtained highly active silicic acid	20.0	20.0
vinyl cyclohexene	—	3.0
di-tertiary butylperoxide	1.5	1.5

10 After vulcanisation at a pressure of 4.0 atm. and a temperature of 151° C. for 30 min. the  
following mechanical values were found:

Tensile strength (kg/cm <sup>2</sup> )	90	169
Elongation (per cent)	250	515
Modulus at 300 per cent elongation (kg/cm <sup>2</sup> )	31	81
Modulus at 500 per cent elongation (kg/cm <sup>2</sup> )	82	135
Hardness at 20° C. (shore)	73	85
at 75° C. (shore)	38	68
Elasticity (per cent) 20° C.	31	54

## EXAMPLE 7

A co-polymer of

- 67.0 parts by weight of ethylene and  
 33.0 parts by weight of propylene  
 5 was mixed with  
 50.0—300.0 parts by weight of S.R.F.  
 carbon black,  
 2.0 parts by weight of di-cumyl per-  
 oxide, and  
 10 3.0 parts by weight of triallyl cyan-  
 urate

and subsequently vulcanised in the press at  
 151° C. for 30 min.

- 15 In all cases non-fusing products of excellent  
 thermal stability and very good mechanical  
 properties, and which were insoluble in or-  
 ganic solvents, were obtained.

## WHAT WE CLAIM IS:—

1. A process for the production of cross-  
 20 linked elastomers, which comprises heating a  
 mixture of (1) a linear co-polymer of ethylene  
 and 10 to 60 per cent by weight of a mono-  
 ethylenically unsaturated monomer containing  
 25 an aliphatic carbon atom having only one  
 hydrogen atom bonded thereto, (2) 1 to 10  
 per cent by weight of said co-polymer of a  
 free-radical forming compound and (3) 0.5 to  
 20 per cent by weight of said co-polymer of  
 a monomer having at least two ethylenically  
 30 unsaturated groups, at a temperature of from  
 50° C. to 250° C.  
 2. A process according to claim 1, wherein  
 said compound (3) is a compound containing  
 at least three allyl groups.

3. A process according to claim 2, wherein 35  
 the co-polymer is a co-polymer of ethylene  
 and a vinyl ester, the vinyl ester content  
 whereof is 20 to 50 per cent.

4. A process according to claim 2, wherein 40  
 the co-polymer is an ethylene-vinyl acetate  
 co-polymer produced by free-radical poly-  
 merisation in a liquid phase containing pre-  
 dominantly tertiary butanol.

5. A process according to claim 1, wherein 45  
 the co-polymer is a co-polymer of ethylene  
 with 10 to 60 per cent of propylene.

6. A process according to any of claims 1  
 to 5, wherein the organic peroxide is one 50  
 which at temperatures up to 100° C. has a  
 half-life period of decomposition of more  
 than 24 hours and which decomposes rapidly  
 above that temperature up to 250° C.

7. A process according to any of claims 1  
 to 6, wherein said compound (3) is triallyl 55  
 cyanurate.

8. A process according to any of claims 1  
 to 6, wherein said compound (3) is triallyl  
 phosphate.

9. A process according to claim 1, sub- 60  
 stantially as described with reference to any  
 of the Examples.

10. Cross-linked elastomers, whenever pro-  
 duced by the process claimed in any of the  
 preceding claims.

ELKINGTON & FIFE,  
 Consulting Chemists and Chartered  
 Patent Agents,  
 Bank Chambers, 329, High Holborn,  
 London, W.C.1,  
 Agents for the Applicants.

THIS PAGE BLANK (ISPTO)